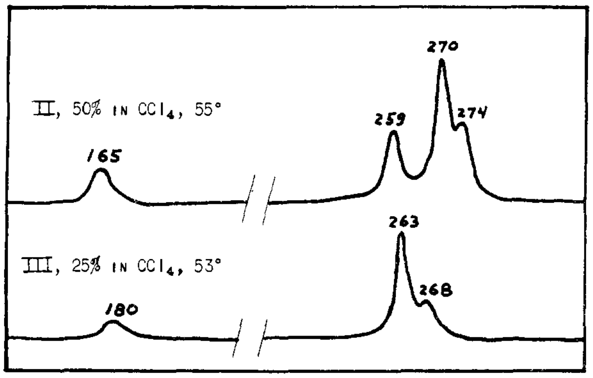
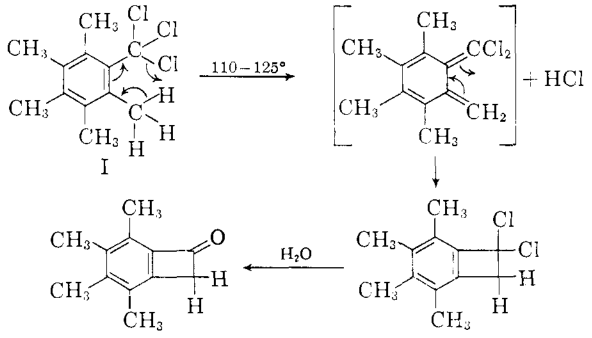


Fig. 1.—Nuclear magnetic resonance spectra at 60 Mc.: numbers are cps. with respect to benzene as an external reference.

C, 62.89; H, 6.16; Cl, 30.95; mol. wt., 229. Found: C, 62.93; H, 6.27; Cl, 30.88; Rast molecular weight (camphor), 201. II gave an immediate precipitate with aqueous-alcoholic silver nitrate; after removing the silver chloride, work-up of the filtrate, or alternatively by direct hydrolysis of II with aqueous acetone, there was obtained in excellent yield a crystalline ketone III, m.p. 153–154° (from ethanol). *Anal.* Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.57; H, 8.16. Oxime, m.p. 173–175°, 2,4-DNP, m.p. 282–283°. III had a carbonyl band at 5.67μ and bands in the ultraviolet (ethanol) at 306 mμ (log ϵ = 3.47) and 265 mμ (log ϵ = 4.18). The n.m.r. spectra of II and III are shown in the figure.[4]

These data are best interpreted in terms of the reaction scheme



From mesitylene, one can obtain a compound presumably analogous to II, m.p. 55–57° (from hexane). *Anal.* Calcd. for $C_{10}H_{10}Cl_2$: C, 59.72; H, 5.01; Cl, 35.26. Found: C, 59.90; H, 5.10; Cl, 35.27.

In a preparative scale experiment, without purification of the intermediate II, an 89% yield of III was obtained from 5 g. of I. This constitutes, then, an excellent preparative procedure for benzocyclobutenones and compounds derived therefrom.[5] Its synthetic utility and the chemistry of the products are being explored.[6,7]

---

[4] We are indebted to Mr. James C. Woodbrey for determining these spectra.

[5] For other benzocyclobutene syntheses, see M. P. Cava and A. A. Deana, THIS JOURNAL, **81**, 4266 (1959), and earlier papers by Cava's group; L. Horner, W. Kirmse and K. Muth, *Chem. Ber.*, **91**, 430 (1958); A. P. terBorg and A. F. Bickel, *Proc. Chem. Soc.*, 283 (1958); and F. R. Jensen and W. E. Coleman, *J. Org. Chem.*, **23**, 869 (1958).

[6] The results of a preliminary deuterium exchange experiment with III are of some interest. III (0.397 g., 1.50 mmoles) dissolved in 4 ml. of D_2O and 6 ml. of ethanol was refluxed for two hours. A 4-ml. sample was quenched in 20 ml. of ice-cold distilled water, and extracted immediately with three 10-ml. portions of pentane. Recovery of III was nearly quantitative; the crystalline product showed considerable C-D absorption at 4.48μ; the carbonyl at 5.7μ was unaltered.

[7] We are indebted to Mr. Frank J. Chloupek for stimulating discussions of this work.

THE KEDZIE CHEMICAL LABORATORY
MICHIGAN STATE UNIVERSITY
EAST LANSING, MICHIGAN
HAROLD HART
RICHARD W. FISH

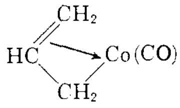
RECEIVED DECEMBER 23, 1959

ALLYLCOBALT CARBONYLS

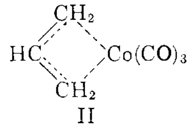
Sir:

We wish to report the formation of a new type of cobalt carbonyl compound, allylcobalt tricarbonyl. When excess $NaCo(CO)_4$ reacts with allyl bromide in ether at 25°, exactly one mole of carbon monoxide is liberated per mole of bromide. Distillation yields a reddish yellow, air-sensitive liquid which can be crystallized from pentane to give a yellow crystalline solid, m.p. −33 to −32°.

Anal. Calcd. for $C_6H_5O_3Co$: CO, 45.6; Co, 32.0. Found CO (by treatment with I_2 in methanol), 44.8; Co, 31.5, 31.1. The compound was shown to be diamagnetic by e.p.r. The n.m.r. spectrum of the allyl compound shows three types of hydrogen in the ratio 2:2:1. Although the spectrum was not sufficiently well resolved to differentiate unequivocally between the unsymmetrical structure I and the symmetrical structure II, the preponderance of evidence would appear to favor the symmetrical structure.[1] Whereas alkylcobalt tetracarbonyls are quite unstable thermally,[2,3] allylcobalt tricarbonyl appears to be stable indefinitely at room temperature.



I



II

The equilibrium mixture of 1-bromo-2-butene and 3-bromo-1-butene reacts with $NaCo(CO)_4$ in an entirely analogous fashion. One mole of carbon monoxide is evolved and distillation yields a red-yellow oil identical with the reaction product of butadiene and $HCo(CO)_4$.[4,5] The compound is presumably 2-butenylcobalt tricarbonyl.[6]

If the reaction of allyl bromide with $NaCo(CO)_4$ is carried out at 0° in the presence of carbon monoxide, about 0.5 mole of carbon monoxide is absorbed. At this point the infrared spectrum of the solution shows a band at 5.8 μ, indicating the presence of an acylcobalt compound.[3] Gas is

---

[1] We are indebted to Dr. J. C. W. Chien for the determination and interpretation of the e.p.r. and n.m.r. spectra.

[2] W. Hieber, O. Vohler and G. Braun, *Z. Naturforsch.*, **13b**, 192 (1958).

[3] R. F. Heck and D. S. Breslow, unpublished work.

[4] H. B. Jonassen, R. I. Stearns, J. Kenttämaa, D. W. Moore and A. G. Whittaker, THIS JOURNAL, **80**, 2586 (1958).

[5] W. W. Prichard, U. S. Reissue 24,653 (1959).

[6] H. B. Jonassen independently has arrived at the same conclusion (London Conference on Coördination Chemistry, April, 1959).

evolved slowly on standing and the spectrum changes to that of I; "crotyl bromide" reacts analogously. That an unstable acylcobalt tetracarbonyl is formed initially in these reactions has been shown by treating $NaCo(CO)_4$ with vinylacetyl chloride at 0°. The initial reaction mixture shows the 5.8 μ band, but on standing about 2 moles of carbon monoxide is evolved and distillation yields pure I. The course of the reaction can be represented by the equations

$$\begin{tikzcd}
 & \text{I} + CO \\
CH_2{=}CHCH_2Br + NaCo(CO)_4 \arrow[r] & CH_2{=}CHCH_2Co(CO)_4 \arrow[u] \arrow[d, shift left, "CO"] \\
CH_2{=}CHCH_2COCl + NaCo(CO)_4 \arrow[r] & CH_2{=}CHCH_2COCo(CO)_4 \arrow[u, shift left, "-CO"]
\end{tikzcd}$$

RESEARCH CENTER
HERCULES POWDER COMPANY
WILMINGTON, DELAWARE

RICHARD F. HECK
DAVID S. BRESLOW

RECEIVED DECEMBER 14, 1959

KINETICS OF THE METAL-AMMONIA-ALCOHOL REDUCTION OF BENZENE

Sir:

In a recent paper[1] we reported (1) that the reduction of benzene with stoichiometric quantities of lithium and ethanol followed over all third-order kinetics, and (2) that the individual orders with respect to alcohol and lithium in the lithium-ammonia-*t*-butyl alcohol reduction of benzene were unity, as determined by the method of initial rates. We concluded[2] that the rate law governing this type of reaction is

$$-d(ArH)/dt = k(ArH)(M)(ROH) \qquad (1)$$

Our evidence has been criticized by Eastham, Keenan and Secor[3] on the grounds that competing hydrogen evolution would invalidate the kinetic analysis in the first of the above studies. However, our preliminary experiments[1] indicated a high yield (94%) of dihydrobenzene from the lithium-ethanol reduction so that the slight downward deviation expected in the third-order plot (visible in our published data) would be insufficient to obscure the third-order adherence.[4]

TABLE I

INITIAL REDUCTION RATES OF BENZENE WITH LITHIUM AND *t*-BUTYL ALCOHOL IN LIQUID AMMONIA-6% ETHYL ETHER

Run	$[C_6H_6]$	[Li]	[*t*-BuOH]	Time in sec.	Moles of dihydrobenzene produced
1[a]	[0.062]	[0.124]	[0.124]	50	0.0023
				100	0.0038
2[a]	[0.124]	[0.124]	[0.124]	50	0.0043
				100	0.0077
3[a]	[0.062]	[0.248]	[0.124]	50	0.0044
				100	0.0080
4[a]	[0.062]	[0.124]	[0.248]	50	0.0046
				100	0.0079

[a] Data quoted under Runs 1 and 2 are averages of duplicate runs. Runs 3 and 4 are single runs; however, *cf.* Table III, reference 1.

We have nevertheless redetermined the orders with respect to the three reactants benzene, lithium, and *t*-butyl alcohol, by the method of initial rates,[5] a method insensitive to the presence of minor side reactions. Experimental techniques were as previously reported.[1]

Our data are presented in Table I. It is observed that doubling the concentration of each reactant doubles the initial reduction rate within experimental error. Therefore, the concentration of each reactant enters the rate law in the first power. Our conclusions based on the previous study are thereby confirmed.

In our study of the effect of proton source, nature of metal, and added salts,[1] the rate constants for the slow reductions with sodium and potassium were calculated from the slopes of third-order plots covering a small fraction of reaction. In these cases, hydrogen evolution can compete more effectively,[2] and the quoted rate constants are probably low by 20-30% for the sodium reductions and by a factor of 2-3 for the potassium reduction.

Our conclusions with respect to mechanism are unaffected by these differences.

Acknowledgment.—We wish to thank Professors J. F. Eastham and C. W. Keenan for making copies of their manuscript available to us before publication.

---

[1] A. P. Krapcho and A. A. Bothner-By, THIS JOURNAL, **81**, 3658 (1959).

[2] The conclusion rested on the basis of the two cited pieces of evidence. No conclusions concerning the form of the kinetic law were drawn from data on reductions with sodium or potassium. These runs were made for the purpose of comparing rates of reduction with different alkali metals, and are discussed in a separate section of our paper.

[3] J. F. Eastham, C. W. Keenan and H. V. Secor, THIS JOURNAL, **81**, 6523 (1959).

[4] We are unable to account for the discrepancy between our findings and that reported by Eastham, *et al.*,[2] who, for lithium reduction, found 12% hydrogen evolution at a time when only 60% of the benzene was reduced. We have repeated their measurements of hydrogen evolution during the sodium-ammonia-ethanol reduction of benzene, using vacuum line techniques in order to reduce initial concentrations of water, oxygen, peroxides, or other catalytic species, and have found 15% hydrogen evolution after 2700 sec. It is not clear, however, whether this lower value reflects lower initial rates of hydrogen evolution, or merely a subsequent deceleration, as noted in an earlier paper (J. F. Eastham and D. R. Larkin, *ibid.*, **81**, 3652 (1959)).

[5] R. Livingston, in "Techniques of Organic Chemistry," Vol. VIII, Interscience Publishers, New York, N. Y., 1953, p. 183 ff.

CHEMISTRY DEPARTMENT
PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA
MELLON INSTITUTE
PITTSBURGH, PENNSYLVANIA

A. P. KRAPCHO
A. A. BOTHNER-BY

RECEIVED DECEMBER 11, 1959

A NEW SYNTHESIS FOR HEXASILICON TETRADECACHLORIDE,[1] Si_6Cl_{14}

Sir:

In the presence of trimethylamine,[2] disilicon hexachloride, Si_2Cl_6, undergoes a quantitative

---

[1] The authors gratefully acknowledge the partial support of this project by a Research Corporation Frederick Gardner Cottrell Grant. This work was presented in part at the 133rd meeting of the American Chemical Society.

[2] With pure Si_2Cl_6 at room temperature a small trace of amine is sufficient. The disproportionation is inhibited by $TiCl_4$ and O_2. These inhibitions can be overcome by the use of larger amounts of amine. In this case, however, the resulting Si_6Cl_{14} is contaminated with titanium complexes or chlorosiloxanes and the net yield is diminished by losses during purification, effected by sublimation *in vacuo* at 125° or by recrystallization from trichlorosilane or diethyl ether solutions